Original Research

Interaction of Liming and Earthworm Humus in Detoxification of Soil Contaminated with Excess Copper

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Abstract

The effect of liming on uptake of copper by white mustard (*Sinapis alba* L.) was evaluated when applied alone or in conjunction with earthworm humus in detoxification of light (sandy) soil polluted with excess copper. The study consisted of two-factor pot trials (first-rate factor – degree of soil contamination: 0, 75, 150, 300, and 450 mg $Cu \cdot kg^{-1}$ of soil; second-rate factor – variants of application of $CaCO_3$ and earthworm humus (EH)). In the absence of any remedial treatment, phytotoxicity of copper at a concentration of 75 mg $Cu \cdot kg^{-1}$ decreased the mustard yield by 60%, while at 150 mg $Cu \cdot kg^{-1}$ the loss of yield was over 90% compared to natural soil. Both $CaCO_3$ and EH reduced Cu uptake. High effectiveness of liming with a $CaCO_3$ dose according to double hydrolytic acidity (2 Hh) in detoxification of the analyzed soil was demonstrated. Simultaneous introduction of EH in the amount of 1.5% of soil weight resulted in Cu uptake reduction and the same metal concentration decrease in plant foliage tissues. The highest value of plant tolerance index (yield on polluted soil/yield on control soil), was obtained under joint application of $CaCO_3$ according to 2 Hh+EH 1.5%. Indices of Cu bioaccumulation (increase of Cu concentration in plant/increase of Cu concentration in soil), tend to decrease as soil contamination increases, implicating a depressed ability of white mustard plants to accumulate this element in its aerial parts.

Keywords: soil detoxification, excess copper, liming, earthworm humus, white mustard

Introduction

Modification of the sorptive complex of sandy soil contaminated with excess trace metals is one of the least expensive soil remediation methods. The materials needed are relatively inexpensive and easily available, yet the possible results are rather satisfactory. The treatments involved most often include liming (exchangeable cations) and adding to soil various types of organic (peat, brown coal, lignite, compost) or inorganic sorbents (clay minerals, zeolites, etc.) [1-3]. Light sandy soils, low in organic matter and clay minerals, are prone to contamination by trace metals. On the other hand, it is easier to improve their sorptive properties. The relevant studies underline good results in soil remediation achieved by using sorbents and simultaneous soil deacidification [4-6]. Earthworm humus (EH) containing humified organic matter possess a high capacity for cationic exchange and for water adsorption. Its molecular structure contains carboxylic acids responsible for the adsorption of heavy metals in a process that involves exchange of protons of weak organic acids for metal ions dissolved in aqueous solutions [7, 8].

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The purpose of this study has been to determine the effectiveness of calcium carbonate and EH applied separately or jointly in detoxification of light acidic soil polluted by excessive amounts of copper.

Experimental Procedures

Design of Experiment

This paper contains a synthesis of the results obtained during two years of two-factor pot trials carried out in four replications. The design of the experiment was as follows: first-rate factor – degree of soil pollution with copper, n=5 (A1 – 0, A2 – 75, A3 – 150, A4 – 300, A5 – 450 mg Cu·kg^{-1} soil dry matter); second-rate factor – soil amendments – $CaCO_3$ and EH combinations, n=6 (B1 – 0; B2 – EH 3% by weight of soil dry matter; B3 – $CaCO_3$ according to 1 hydrolytic acidity (1 Hh); B4 – $CaCO_3$ according to 2 Hh; B5 – $CaCO_3$ according to 1 Hh+EH 3%; B6 – $CaCO_3$ according to 2 Hh+EH 1.5%. The dose of $CaCO_3$ determined according to single hydrolytic acidity (1 Hh) amounted to 1.10 g·kg^{-1} of the soil.

Soil, Plants and Treatment Procedures

Wagner's type pots containing 6 kg of soil were used. The haplic luvisols soil used for the experiments was loamy sand in texture (17% fraction <0.02 mm), acidic in reaction (pH_{KCl} 5.5), and moderately abundant in available forms of P, K, Mg, Cu, Mn, Mo, and Zn, but low in B [9].

The test plant was cv. Salvo white mustard (*Sinapis alba* L.) grown as an aftercrop after spring triticale (*Triticosecale* Witt.). Both copper in the form of a solution of $CuSO_4{\cdot}5H_2O$ and soil remediation treatments were applied before sowing the main crop (triticale). The soil was carefully mixed with amounts of $CuSO_4{\cdot}5H_2O$ solution appropriate for subblocks A2, A3, A4, and A5, and incubated for 14 days, maintaining soil moisture at 60% of maximum water capacity. Afterward, the soil was carefully mixed with $CaCO_3$ and humus, according to the experimental design, and placed in pots. EH of pH_{KCl} 6.2 containing 21.6% of organic substance was produced by California earthworms (*Eisenia foetida*) from cattle manure. Apart from the basic fertilization under main crop (triticale), in the amounts commonly used in pot trials (except Cu), mustard was nourished with nitrogen by adding 0.6 g N per pot. During the growing season, the moisture of the soil in the pots was kept at 60% maximum water capacity.

Harvest, Sample Collection and Chemical Analyses

Before experiment, soil texture, pH in 1 mol KCl·dm^{-3}, hydrolytic acidity and content of available forms of P, K, Mg, B, Cu, Mn, Mo, and Zn were determined.

Aerial parts of mustard were harvested during the growth phase preceding the flowering stage, and their green mass for each experimental object was weighed. The concentration of copper in plants was determined, while the soil was tested for pH_{KCl}, content of available forms of copper, and organic carbon. The chemical tests of the soil and plants were performed in the IUNG-PIB Main Laboratory for Chemical Analyses in Puławy, with the methods used at Polish agrochemical stations [10].

Statistical Procedures and Indexes

The results obtained in the experiment underwent statistical processing with analysis of variance, correlation, and stepwise multiple regression being completed.

For evaluation of the phytotoxic effect produced by excess copper in soil on volume of yields, plants' tolerance index (T_I) was applied, where T_I = weight of yield from polluted soil to yield from the control soil (A1). Values of T_I<1 mean that the yield has been diminished due to the phytotoxic effect produced by a metal. Copper concentration (C_I) and bioaccumulation (B_I) indices were also calculated. The C_I indices express the ratio of the content of a metal in plants from contaminated soil to its content in plants grown on control soil. B_I index is a ratio of the increase of metal content in plants to its increase in soil and, as such, it reflects the metal's ability to migrate from soil to plant tissues [11, 12].

Results and Discussion

Effect of Cu Phytotoxicity on Mustard Yield

When no soil remediation was applied, the phytotoxicity of copper at its lowest soil content (A2 – 75 mg Cu·kg^{-1}) caused a large yield loss (T_I=0.66). In subblock A3 (150 mg Cu·kg^{-1}), T_I was observed to fall down to 0.08, while at higher copper levels (subblocks A4 and A5), the yield was reduced completely.

The phytotoxicity of copper is clearly reflected by high coefficients of the correlations: yield mass/available Cu in soil r=-0.764, and yield mass/Cu in plant r=-0.843, p=0.001. The applied liming treatments (according to 1 and 2 Hh) in subblock A3 helped to significantly recover the soil's yield-forming potential (T_I=0.48 and 0.51), although when copper contamination was higher the effect of this treatment, analogously to soil amendment with humus, was statistically non-significant (T_I=0.01-0.02). At all levels of copper contamination, the most effective method for detoxication of the analyzed soil proved to be a combination of liming and EH (Table 1). When these two techniques were combined, between 16% (A5, soil most heavily polluted with copper, 450 mg Cu·kg^{-1}) to 73% (A2 – 75 mg Cu·kg^{-1}) of yields from natural soil were recovered. The results indicate high effectiveness of remediation by improving the reaction of copper-contaminated soil combined with soil amendment with organic sorbents as in previous reports [4, 5, 13]. The interaction of these two factors, however, depends on the type of organic substance added to soil. In a study completed by Adhikari and Mandal [6], introduc-

Table 1. Yield of white mustard aerial parts (g·pot^{-1}) and plant tolerance index (T_I).

Second-rate factor**	First-rate factor variants*								
	A1	A2		A3		A4		A5	
	g·pot^{-1}	g·pot^{-1}	T_I	g·pot^{-1}	T_I	g·pot^{-1}	T_I	g·pot^{-1}	T_I
B1	106.2	70.5	0.66	8.8	0.08	-	-	-	-
B2	139.3	84.4	0.61	41.4	0.30	21.0	0.15	1.2	0.01
B3	136.2	79.1	0.58	65.7	0.48	16.8	0.12	2.0	0.01
B4	140.9	90.8	0.64	72.4	0.51	27.9	0.20	9.8	0.07
B5	146.9	102.4	0.70	84.2	0.57	43.9	0.30	19.7	0.13
B6	166.2	120.6	0.73	105.9	0.64	57.6	0.35	27.2	0.16

$LSD_{(yield)}$ p=0.01; B/A=36.1; A/B=29.5

*first-rate factor – degrees of soil contamination with copper, n=5 (A1 – 0, A2 – 75, A3 – 150, A4 – 300, A5 – 450 mg Cu·kg^{-1} dry matter of soil)

**second-rate factor – $CaCO_3$ and EH combinations, n=6 (B1 – 0; B2 – EH 3% of soil dry matter weight; B3 – $CaCO_3$ according to 1 hydrolytic acidity (1 Hh); B4 – $CaCO_3$ according to 2Hh; B5 – $CaCO_3$ according to 1 Hh+EH 3%; B6 – $CaCO_3$ according to 2 Hh+EH 1.5%.

tion of cellulose as an organic sorbent to soil polluted with excess copper, previously limed, caused mobilization of copper in the form of organic complexes potentially available to plants.

Bioavailability and Uptake of Cu by Mustard Plants

In the present study, the highest Cu concentration in mustard plants (55.2 mg Cu·kg^{-1}) was found in A4B3 treatment ($CaCO_3$ according to 1 Hh/300 mg Cu·kg^{-1}) (Fig. 1). At this nearly 13-fold increase in the Cu content compared to the initial concentration (A1B3), in both years of the experiment, the smallest yields (on average 16.8 g·pot^{-1}) were obtained (Table 1). The negative influence of copper bioaccumulation is expressed by the multiple equation with a relatively high determination coefficient:

$$y_{yield}=138.06-0.21Cu_{plant}-0.03Mn_{plant} \quad (1)$$
$$R^2=0.726;\ p=0.001$$

...where: y – green matter yield, Cu_{plant} – mg Cu·kg^{-1} plants' dry matter, Mn_{plant} – mg Mn·kg^{-1} plants' dry matter.

Including Mn in the equation with a negative sign should be explained by the alkalizing effect of the applied $CaCO_3$. This type of change in soil reaction could generate some shortages of manganese with a negative impact on crop yields (a "–" sign in the equation), visible in the chemical composition of plants.

In order to attain a more complete evaluation of the interaction between soil contamination and the applied remediation treatments with respect to the level of copper accumulation in plants, copper concentration indices (C_I) also were calculated. An increase in C_I is suggestive of the appearance of such conditions that favour the bioaccumula-

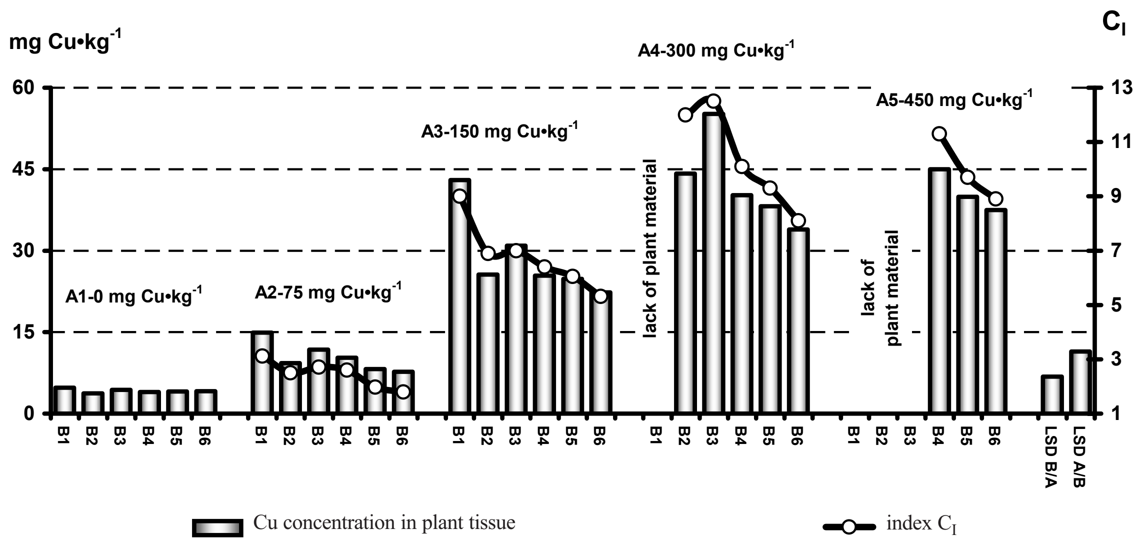

Fig. 1. Indices of copper concentrations (C_I) against metal content in the white mustard aerial parts.
$LSD_{(Cu\ concentration)}$ p=0.01; B/A=6.81, A/B=11.44

tion of a given element [11]. In our investigations, such conditions became more evident as the Cu level in soil increased. A decrease in the C_I value that appeared when an applied remediation technique was more effective testifies to the fact that a combination of calcium carbonate and EH (B5 and B6 treatments) was the most effective technique (Fig. 1).

In our evaluation of the soil/plant relationship, bioaccumulation index (B_I) was also involved. The limited ability of mustard to accumulate copper in aerial parts was revealed owing to a gradually decreasing value of B_I under increasing soil contamination (subblocks A4, A5) (Fig. 2). The B_I value was drastically lower in B5 and B6 treatments at all levels of soil pollution, which reflects the effectiveness of the joint application of $CaCO_3$ and EH in restricting the transfer of copper from soil to plants. The above relationships are confirmed by the correlations: Cu_{soil}/Cu_{plant} r=0.888 and $pH_{KCl\ soil}/Cu_{plant}$ r=-0.579 (p=0.001). The copper uptake with the mustard yield as a result of the degree of soil contamination and effectiveness of remediation was the highest in subblock A3, in which soil was moderately polluted (150 mg $Cu{\cdot}kg^{-1}$). But even the highest value of copper uptake determined in subblock A3B5 (254.0 μg $Cu{\cdot}pot^{-1}$) corresponded to just 0.028% of the amount introduced to the soil of this treatment (900 $mg{\cdot}pot^{-1}$) (Fig. 2).

Impact of the Remedial Treatment on Soil Properties

Very low initial carbon content in the soil and its acidic reaction were certainly the main factors promoting copper bioavailability. As a result of the remediation treatments applied, the pH of the soil rose considerably, even by 2 units, and so did the content of organic carbon. The improved soil reaction and richer organic carbon content in soil were accompanied by a depressed amount of available copper, determined in 1 mol $HCl{\cdot}dm^{-3}$. The chemical analysis of soil after mustard harvest (extraction in 1 mol $HCl{\cdot}dm^{-3}$) showed between 68 and 95% of the copper introduced to the soil, with lower percentages determined in the soil where $CaCO_3$ and humus were applied in conjunction (Table 2).

It was possible to present the phytotoxicity of excess soil copper and the positive impact of improved soil pH and soil enrichment with organic substance as multiple regression equations:

$$y_{yield}=-58.02-0.24Cu_{soil}+19.07\ pH_{soil}+26.34C_{soil}$$
$$R^2=0.525;\ p=0.001 \qquad (2)$$

...where: Cu_{soil} – content of available copper in mg $Cu{\cdot}kg^{-1}$ of soil, pH_{soil} – pH of soil determined in 1 mol $KCl{\cdot}dm^{-3}$, C_{soil} – percentage of organic carbon determined with Tiurin's method.

Our experiment has verified and supported the claim presented in many reports, stating that soil reaction has the strongest influence on the immobilization of excess copper in mineral soils [14-17].

Lombi et al. [18] in soils treated with lime have found significant amounts of nonlabile (fixed) Cu to be associated with colloids <0.2 μm in the soil solution phase. However, when the soils were re-acidified, the labile pool of metals increased sharply.

In general, sorption of copper increases as pH value increases. But solubility of the metal may increase at higher pH as well, due to binding with dissolved organic matter. This is attributed to the formation of soluble Cu-organic complexes. As Zhou and Wong [19] report, the addition of dissolved organic matter derived from sludge reduced the sorption of Cu by a calcareous soil at pH>6.8.

The results of our experiment demonstrate that soil remediation with the lower $CaCO_3$ dose (according to 1 Hh) was less successful than the application of EH alone in a dose corresponding to 3% of soil weight. Translocation of Cu from soil to plants, expressed through the bioaccumulation index (B_I), clearly demonstrates that humus is more effective in this respect, thus supporting the importance of

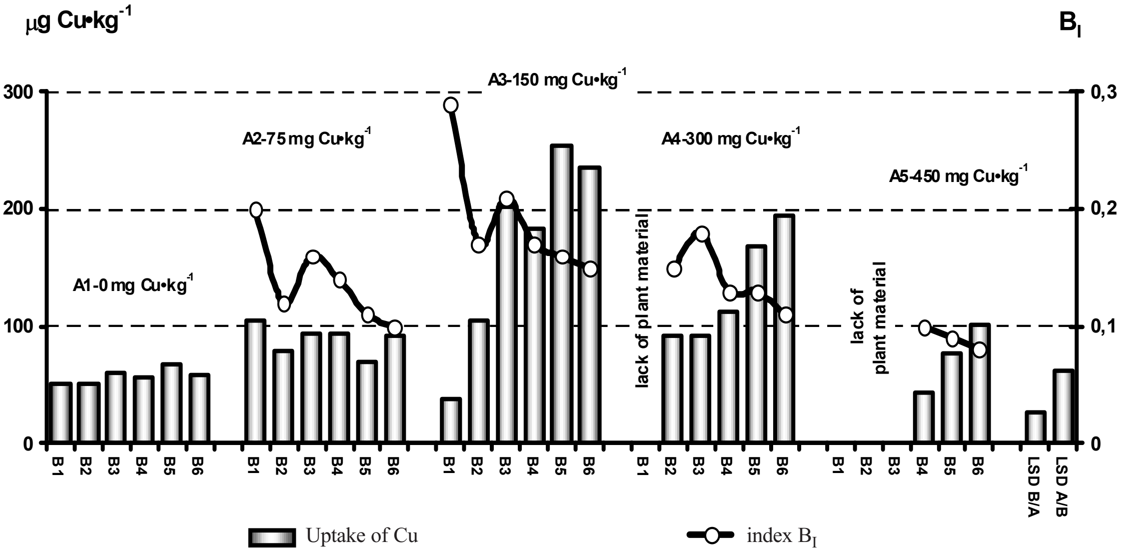

Fig. 2. Index of copper bioaccumulation (B_I) against Cu uptake by white mustard yield.
$LSD_{(Cu\ uptake)}$ p=0.01; B/A=27.21, A/B=63.09

Table 2. Reaction (pH_{KCl}), available copper (mg Cu·kg^{-1}), and organic carbon (C_{org}-%) in soil after mustard harvest.

Soil contamination level (first-rate factor)		Soil amendments (second-rate factor)					
		B1	B2	B3	B4	B5	B6
		0	EH 3%	$CaCO_3$ 1 Hh	$CaCO_3$ 2 Hh	EH 3%+$CaCO_3$ 1 Hh	EH 1.5%+$CaCO_3$ 2 Hh
A1 0 mg Cu·kg^{-1}	pH	5.4	5.7	6.5	7.0	6.6	6.9
	Cu	5.5	4.8	4.2	3.9	3.9	4.3
	C	0.8	1.1	0.9	1.0	1.1	1.1
A2 75 mg Cu·kg^{-1}	pH	5.4	5.5	6.8	7.4	6.6	7.3
	Cu	71.4	66.5	67.5	66.0	63.2	62.1
	C	0.8	1.0	0.8	0.8	1.0	0.9
A3 150 mg Cu·kg^{-1}	pH	5.4	5.4	6.0	7.1	6.2	7.3
	Cu	125. 0	110.0	118.0	115.0	102.0	105.0
	C	0.8	1.0	0.8	0.8	1.0	1.0
A4 300 mg Cu·kg^{-1}	pH	5.0	5.1	5.9	7.1	6.1	7.2
	Cu	270.0	216.0	236.0	235.0	215.0	221.0
	C	0.7	0.9	0.7	0.8	1.0	0.9
A5 450 mg Cu·kg^{-1}	pH	5.0	4.9	5.6	6.8	6.0	7.1
	Cu	351.0	354.0	366.0	374.0	351.5	324.0
	C	0.7	0.9	0.7	0.7	0.9	0.8

$LSD_{(available\ copper)}$ p=0.01; B/A=16.35; A/B=55.73
$LSD_{(organic\ carbon)}$ p=0.01; B/A=0.17; A/B=non-significant difference

organic matter for the stabilization of soil copper [20-24]. The most successful solution, also indicated in other papers [4, 6, 21], proved to be combinations of both treatments.

In an experiment carried out by Alvarenga et al. [5], joint application of municipal solid waste compost and liming materials led to a decrease in the mobile fractions of Cu, but mobilizable fractions of Cu increased with separate compost application.

Neaman et al. [25] in a study on sandy loam texture soil, polluted with copper (310-640 mg·kg^{-1}) stated that in solutions percolating through the soil during rain events, dissolved organic carbon was the major factor controlling total dissolved copper concentrations, while soil pH was the major factor controlling free Cu^{2+} activity.

Practicability of the remediation method of light soil contaminated with excess copper involving joint applications of EH and $CaCO_3$ should be tested under field conditions.

Conclusions

1. In the absence of remediation, phytotoxicity of excess copper in the sandy soil of acid reaction limited the yields of white mustard in proportion to the level of contamination. When pollution was higher than 150 mg Cu·kg^{-1} of soil, yield was reduced completely.
2. Studies have shown that there is a possibility of detoxification of soil contaminated with copper, and thus recovering lost yields from 16% (for the most contaminated soil – 450 Cu·kg^{-1} of soil) to 73% (at the lowest level of contamination of 75 mg Cu·kg^{-1}) – yields from natural soil (control).
3. High effectiveness of soil liming with a dose of $CaCO_3$ according to 2 Hh in detoxication of the analyzed soil has been shown. The effectiveness of this treatment was improved when EH at 1.5% of soil weight was additionally introduced, as indicated by the values of plant tolerance index T_I.
4. The multiple regression calculations show that improved soil reaction and higher content of organic matter in soil are direct factors leading to detoxification of polluted soil.
5. The decreasing values of copper bioaccumulation index (B_I) as soil contamination degree rose indicate that white mustard has a limited ability to accumulate this metal in aerial parts.

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